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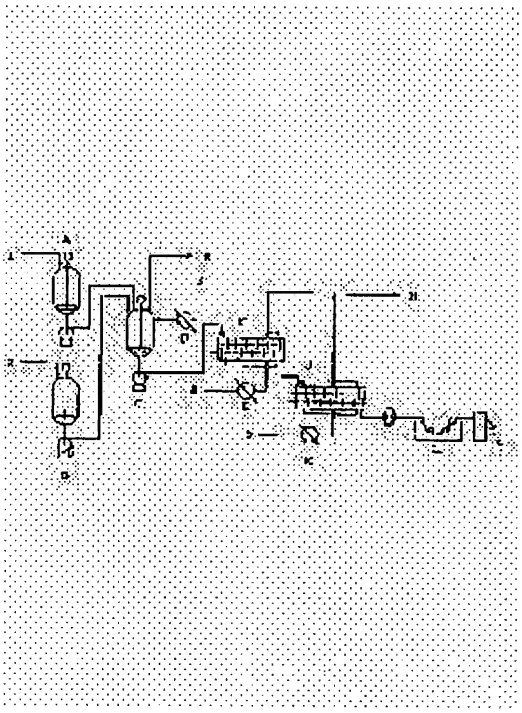
(54) PRODUCTION OF POLYCARBONATE

(57)Abstract:

PURPOSE: To efficiently obtain the subject polymer having excellent hue and strength by transesterifying a dihydric hydroxy compound with a carbonate compound while changing the reaction temperatures of a first reaction zone and a second reaction zone and supplying an inert gas.

CONSTITUTION: (A) A dihydric hydroxy compound (e.g. bisphenol A) 1 and (B) a carbonate compound (e.g. diphenyl carbonate) 2 are melted in melting tanks A and B, supplied to a first reaction tank C, an inert gas 3 in a ratio of the gas to the component A of 0.01-20 by weight is fed to the first reaction tank at 100-280°C reaction temperature and transesterification reaction is carried out to form a reaction mixture containing a low-molecular weight carbonate having 1,000-25,000 viscosity-average molecular weight. Then the reaction mixture is sent to the second reaction tank, the reaction temperature is made higher than that of the first reaction tank, an inert gas 4 in the ratio of the gas to the component A of 0.002-10 by weight is supplied to the reaction tank at 200-350°C and transesterification reaction is carried out to give a polycarbonate having 10,000-50,000 viscosity-average molecular weight.



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* NOTICES *

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DETAILED DESCRIPTION

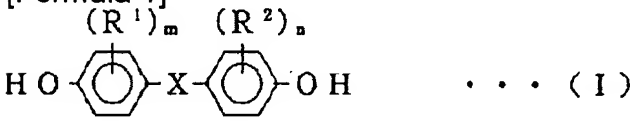
[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the manufacture approach of a new polycarbonate. It is related with the manufacture approach that the polycarbonate which supplied inert gas in the first reaction band and the second reaction band, performed the ester exchange reaction in the ester interchange method in more detail, and was excellent in the hue or the mechanical strength can be obtained efficiently.
[0002]
[Description of the Prior Art] Polycarbonate resin is excellent in mechanical strengths, such as thermal resistance and shock resistance, transparency, etc., and is used as engineering plastics in an optic, a machine part, the electrical and electric equipment and electronic parts, autoparts, and a field with various, still more various containers etc. As the manufacture approach of polycarbonate resin of having such a property, the interfacial polycondensation method, the solution method, the ester interchange method, etc. are learned. In these, a phosgene is used for an interfacial polycondensation method and a solution method, and they have the problem of the methylene chloride used as a solvent remaining. On the other hand, although the above problems do not have an ester interchange method, an ester exchange reaction is performed at an elevated temperature, and it has a mechanical problem. The problem which must remove the phenol generated by the ester exchange reaction, the problem which deterioration of the quality by the elevated temperature tends to generate are in coincidence. Before, examination is variously made by solution of the trouble in the manufacture approach of the polycarbonate by the ester interchange method. For example, the amelioration technique from the format of equipment is indicated by JP,52-36159,B, JP,2-86618,A, and the 2-153923 official report. Moreover, the amelioration technique about the ingredient of equipment is indicated by JP,4-72327,A. furthermore, the solid-state-polymerization method for preventing quality degradation by the elevated temperature in JP,1-158033,A and a 3-59028 official report -- an indication -- now, although it is, actuation of crystallization is needed, and a reaction rate is slow, and it has a problem for productivity. And by the ester interchange method, in order to remove the phenol to generate, a high vacuum is needed and actuation becomes very difficult industrially. Moreover, mixing of air cannot be prevented completely but it is easy to become the factor of coloring by oxidation degradation. For this reason, nitrogen gas is conventionally used for the system of reaction, and a device which solves the problem of coloring is performed.
[0003]
[Means for Solving the Problem] In view of the above-mentioned situation, this invention persons canceled the trouble of the conventional method in an ester interchange method, and repeated research wholeheartedly that the manufacture approach that the polycarbonate excellent in the hue or the mechanical strength can be obtained efficiently should be

developed. Consequently, it found out that the polycarbonate equipped with the target physical properties could be manufactured efficiently by changing the reaction temperature of the first reaction band and the second reaction band, supplying inert gas continuously or intermittently only not only in the purpose of deoxidation, and advancing an ester exchange reaction. This invention is made based on such knowledge. And a bivalence hydroxy compound is received in inert gas. namely, this invention -- the first reaction band -- it is -- (A) bivalence hydroxy compound and (B) carbonate compound -- the reaction temperature of 100-280 degrees C -- The reaction mixture with which 0.01-20 (weight ratio) supply is carried out, an ester exchange reaction is carried out and viscosity average molecular weight contains the low-molecular-weight polycarbonate of 1,000-25,000 is made to generate. Subsequently In the second reaction band, it is higher than the first reaction band in the reaction temperature of the above-mentioned reaction mixture, and a bivalence hydroxy compound is received in inert gas at 200-350 degrees C. The manufacture approach of the polycarbonate characterized by carrying out 0.002-10 (weight ratio) supply, and carrying out an ester exchange reaction and viscosity average molecular weight manufacturing the polycarbonate of 10,000-50,000 is offered.

[0004] First, in this invention, as a bivalence hydroxy compound of the (A) component, there are various kinds of things, for example, an aromatic series dihydroxy compound and an aliphatic series dihydroxy compound can be used. For example, as an aromatic series dihydroxy compound, it is usually a general formula (I).

[0005]

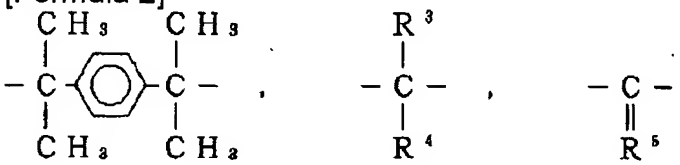
[Formula 1]



・・・(I)

[0006] R1 and R2 are the alkyl groups of a halogen atom (for example, chlorine, a bromine, a fluorine, iodine) or carbon numbers 1-8 among [type, respectively, when this R1 and R2 are plurality, they may be the same, you may differ and m and n are the integers of 0-4, respectively. X -- single bond, the alkylene group of carbon numbers 1-8, the alkylidene radical of carbon numbers 2-8, the cyclo alkylene group of carbon numbers 5-15, the cyclo alkylidene radical of carbon numbers 5-15 or -S-, -SO-, and - SO2-, -O-, -CO-association, or general formula (II) [0007 --]

[Formula 2]



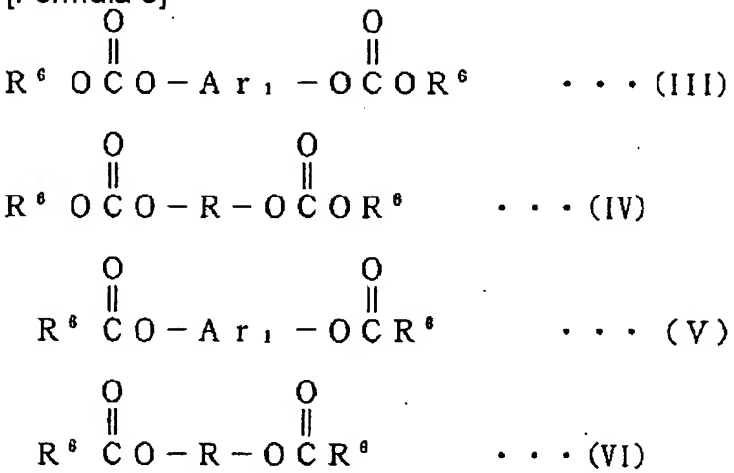
[0008] (-- among a formula, R3 and R4 are a hydrogen atom or a univalent hydrocarbon group, respectively, and R5 is a divalent hydrocarbon group.) -- association expressed is shown.] It comes out and the compound expressed is mentioned. Although there are various things as a compound expressed with the above-mentioned general formula (I), 2 and 2-screw (4-hydroxyphenyl) propane [common-name:bisphenol A] is suitable especially. As aromatic series dihydroxy compounds other than bisphenol A For example A screw Methane; 1 and 1-screw (4-hydroxyphenyl) Ethane; 2 and 2-screw (4-hydroxyphenyl) Butane; 2 and 2-screw (4-hydroxyphenyl) Octane; 2 and 2-screw (4-hydroxyphenyl) Phenylmethane; 2 and 2-screw (4-hydroxyphenyl) Propane; A screw (4-hydroxy-1-methylphenyl) Naphthyl methane; 1 and 1-screw (4-hydroxyphenyl) Propane; (4-hydroxy-t-buthylphenyl) 2 and 2-screw Propane; (4-hydroxy-3-BUROMO phenyl) 2 and 2-screw Propane; (4-hydroxy - 3, 5-tetramethyl phenyl) 2, 2-screw (4-hydroxy-3-chlorophenyl) propane;2, and 2-screw (4-hydroxy - 3, 5-tetra-

chlorophenyl) propane; Screw (hydroxy aryl) alkanes, such as 2 and 2-screw (4-hydroxy - 3, 5-tetrabromo phenyl) propane 1, 1-screw (4-hydroxyphenyl) cyclopentane;1, and 1-screw (4-hydroxyphenyl) cyclohexane; 1 and 1-screw (4-hydroxyphenyl) - Screw (hydroxy aryl) cycloalkanes, such as a 3, 5, and 5-trimethyl cyclohexane 4 4'-dihydroxy phenyl ether; Dihydroxy aryl ether, such as 4, 4'-dihydroxy -3, and the 3'-dimethylphenyl ether, 4 4'-dihydroxydiphenyl sulfide; Dihydroxy diaryl sulfides, such as 4, 4'-dihydroxy -3, and a 3'-dimethyl diphenyl sulfide 4 4'-dihydroxydiphenyl sulfoxide; Dihydroxy diaryl sulfoxides, such as 4, 4'-dihydroxy -3, and a 3'-dimethyl diphenyl sulfoxide 4 4'-dihydroxy diphenylsulfone; dihydroxydiphenyl, such as 4, 4'-dihydroxy -3, and dihydroxy diaryl sulfones, such as - dimethyl diphenylsulfone, 3 '4, 4'-JIHIROKISHI diphenyl, is mentioned. moreover, except for the aromatic series dihydroxy compound expressed with this general formula (I) -- ethoxylation [of dihydroxybenzene such as hydroquinone, resorcinol, and a methyl hydroquinone, and a phenol], or propoxy metaplasia product, for example, screw,-oxy-ethyl-bisphenol A; screw-oxy-ethyl -- dihydroxy naphthalene, such as - tetra-chloro bisphenol A; screw-oxy-ethyl-tetra-chlorohydroquinone, 1, 5-dihydroxy naphthalene;2, and 6-dihydroxy naphthalene, is mentioned.

[0009] And there are various kinds of things as an aliphatic series dihydroxy compound. For example Butane -1, 4-diol; 2,2-dimethyl propane -1, 3-diol; A hexane -1, 6-diol; Diethylene-glycol; Triethylene glycol; Tetraethylene glycol; 2-screw - OKUTA ethylene glycol; -- dipropylene glycol; -- N, the N-methyldiethanolamine; cyclohexane -1, the 3-diol; cyclohexane - 1, 4-diol;1, and 4-dimethylol cyclohexane;p-xylylene glycol;2 -- Ethoxylation of a (4-hydroxy cyclohexyl)-propane and dihydric alcohol or a propoxy metaplasia product is mentioned.

[0010] moreover -- this invention -- as a bivalence hydroxy compound -- general formula (III) - (VI [0011])

[Formula 3]



$$R^6\ OCO-Ar_1-OCOR^6 \quad \cdots (III)$$

$$R^6\ OCO-R-OCOR^6 \quad \cdots (IV)$$

$$R^6\ CO-Ar_1-OCR^6 \quad \cdots (V)$$

$$R^6\ CO-R-OCR^6 \quad \cdots (VI)$$

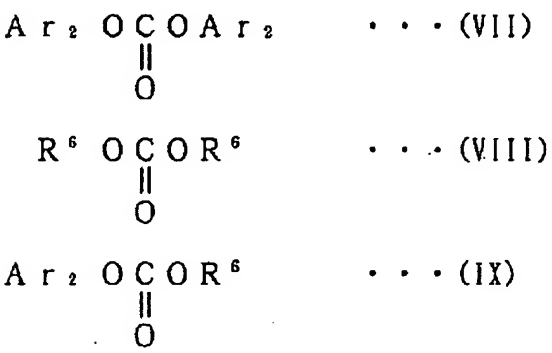
[0012] Ar1 shows the residue excluding two hydroxyl groups from the aromatic series dihydroxy compound among [type. Moreover, R shows the residue excluding two hydroxyl groups from the aliphatic series dihydroxy compound. R6 The cycloalkyl radical which has the alkyl group or 4-7 carbon atoms which have 1-6 carbon atoms is shown.] It can come out and bis-ESURU of an aromatic series dihydroxy compound expressed, bis-ESURU of an aliphatic series dihydroxy compound, the carbonate of an aromatic series dihydroxy compound, or the carbonate of an aliphatic series dihydroxy compound can be used. These bivalence hydroxy compounds may be used independently, respectively, and may be used combining two or more sorts.

[0013] On the other hand, although the carbonate compound of the (B) component has various things in this invention, it is a general formula (VII) preferably. They are the carbonic acid diaryl

compound expressed, the carbonic acid dialkyl compound expressed with a general formula (VIII), or the carbonic acid alkyl aryl compound expressed with a general formula (IX). Here, above-mentioned general formula (VII) - (IX) is expressed as follows.

[0014]

[Formula 4]



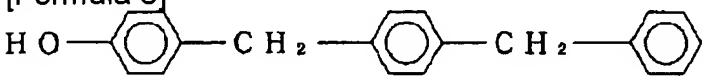
[0015] R6 is the same as the above among [type, and Ar2 shows an aryl group.] The above-mentioned general formula (VII) As a carbonic acid diaryl compound expressed, diphenyl carbonate, JITORIRU carbonate, m-cresyl carbonate, dinaphthyl carbonate, screw (diphenyl) carbonate, etc. are mentioned, for example. Moreover, as a carbonic acid dialkyl compound expressed with the above-mentioned general formula (VIII), dimethyl carbonate, diethyl carbonate, dibutyl carbonate, dicyclohexyl carbonate, etc. are mentioned, for example. And as a carbonic acid alkyl aryl compound expressed with the above-mentioned general formula (IX), methylphenyl carbonate, ethyl phenyl carbonate, buthylphenyl carbonate, cyclohexyl phenyl carbonate, etc. are mentioned, for example. These carbonate compounds may be used independently, respectively and may be used combining two or more sorts.

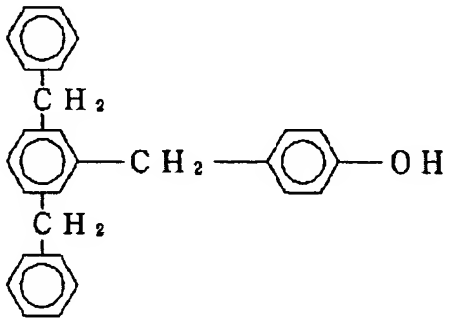
[0016] In this invention, in performing an ester exchange reaction using said bivalence hydroxy compound and carbonate compound, an ester interchange catalyst is not necessarily required, but it is desirable to use it. Here, as an ester interchange catalyst, they are the simple substance of alkali metal or alkaline earth metal, an oxide, a hydroxide, an amide compound, an alcoholate, a phenolate, or ZnO, PbO and Sb 2O3, for example. Concomitant use system catalysts, such as basic metallic compounds [like], an organic titanium compound, a fusibility manganese compound, acetate of calcium, Mg, Zn, Pb, Sn, Mn, Cd, and Co or a nitrogen-containing basicity compound, a boron compound and a nitrogen-containing basicity compound, alkali (earth) metallic compounds, and a boron compound, etc. are mentioned. Moreover, you may be a solid catalyst containing ion exchange resin or an inorganic ion exchanger. These catalysts may be used independently, respectively and may be used combining two or more sorts. The zero to ten - one mol of the amount of the catalyst used can usually be preferably used in zero to ten - two mols to a bivalence hydroxy compound. If this amount used exceeds ten - one mol, it will have a bad influence on degradation and the mechanical physical properties of quality according to the catalyst which remains in a polymer.

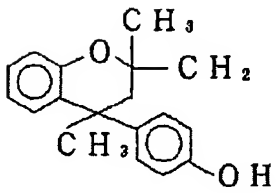
[0017] Moreover, in this invention, although especially limitation is not carried out, it can usually use various kinds of things used for the polymerization of a polycarbonate as an end halt agent. As the end halt agent, specifically as monohydric phenol For example A phenol, o-n-butylphenol, m-n-butylphenol, p-n-butylphenol, o-isobutyl phenol, m-isobutyl phenol, p-isobutyl phenol, o-t-butylphenol, m-t-butylphenol, p-t-butylphenol, an o-n-pentyl phenol, a m-n-pentyl phenol, a p-n-pentyl phenol, an o-n-hexyl phenol, a m-n-hexyl phenol, a p-n-hexyl phenol, p-t-octyl phenol, o-cyclohexyl phenol, m-cyclohexyl phenol, p-cyclohexyl phenol, o-phenylphenol, m-phenylphenol, p-phenylphenol, o-n-nonyl phenol, m-nonyl phenol, p-n-nonyl phenol, o-cumyl phenol, m-cumyl phenol, p-cumyl phenol, o-naphthyl phenol, m-naphthyl

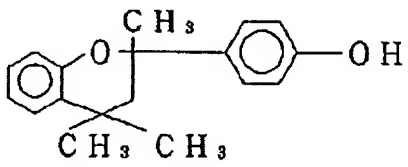
phenol, p-naphthyl phenol;2, 5-G t-butylphenol; 2 and 4-G t-butylphenol; 3, 5-G t-butylphenol;2, 5-JIKUMIRU phenol;3, 5-JIKUMIRU phenol; p-cresol, a BUROMO phenol, tribromophenol, etc. are mentioned. In addition, formula (IV) [0018]

[Formula 5]









[0019] It comes out and the monohydric phenol expressed is mentioned. These monohydric phenol may be used independently, respectively and may be used combining two or more sorts. And in these monohydric phenol, p-t-butylphenol, p-cumyl phenol, p-phenylphenol, etc. are used preferably. As a branching agent, in addition, for example 1, 1, and 1-tris Ethane;alpha, alpha', alpha"-tris (4-hydroxyphenyl) (-- four - hydroxyphenyl --) - one -- three -- five - triisopropyl -- benzene --; -- one - [-- alpha - methyl - alpha - (4'-hydroxyphenyl) -- ethyl --] - four - [-- alpha -- ' -- alpha -- ' - a screw (4"-hydroxyphenyl) -- ethyl --] -- benzene --; -- FURORO -- a glycine -- trimellitic acid -- an isatin screw (o-cresol) etc. -- the compound which has three or more functional groups can also be used.

[0020] Furthermore, a carbonic acid diester compound can be used as other end halt agents according to a situation. As an end halt agent of such a carbonic acid diester compound For example KARUBOBUTOKISHI phenyl phenyl carbonate, methylphenyl buthylphenyl carbonate, ethyl phenyl buthylphenyl carbonate, dibutyl diphenyl carbonate, biphenyl phenyl carbonate, JIBIFE nil carbonate, Walnut phenyl phenyl carbonate, JIKURUMI phenyl carbonate, naphthylphenyl phenyl carbonate, dinaphthyl phenyl carbonate, KARUBO propoxy phenyl carbonate, KARUBO heptoxy phenyl carbonate, KARUBO methoxy-t-buthylphenyl phenyl carbonate and cull BOPURO -- an ibis -- CIF, nil MECHIRUFU, nil phenyl carbonate, chromanyl phenyl carbonate, JIKUROMA nil carbonate, etc. are mentioned.

[0021] Although the manufacture approach of this invention blends said end halt agent or catalyst if needed and obtains a polycarbonate by the ester interchange method using said bivalence hydroxy compound and carbonate compound, it is characterized by changing reaction temperature for this ester exchange reaction in the first reaction band and the second reaction band, supplying inert gas continuously or intermittently, and advancing a reaction. Namely, are in charge of an ester exchange reaction. It is a raw material. (A) An aromatic series dihydroxy compound, an aliphatic series dihydroxy compound, The bivalence hydroxy compound which are the bis-ester of an aromatic series dihydroxy compound, the bis-ester of

an aliphatic series dihydroxy compound, the carbonate of an aromatic series dihydroxy compound, or carbonate of an aliphatic series dihydroxy compound, (B) To a bivalence hydroxy compound, the ratio of the carbonate compound which is a carbonic acid diaryl compound, a carbonic acid dialkyl compound, or an alkyl carbonate Atar compound blends a carbonate compound so that it may become a mol 1 - 1.5 times. In addition, the 1.02 to 1.20 time mol of extent which the amount of a carbonate compound makes superfluous somewhat to a bivalence hydroxy compound according to a situation is desirable. Since viscosity of an ester exchange reaction is low in early stages and viscosity becomes high in the second half, in this invention, it carries out more than the first reaction band, the second reaction band, or it, and a reaction is advanced using the equipment suitable for each. In this case, in the first reaction band, a usual stirred tank and a usual horizontal-type agitator can be used. Moreover, in the second reaction band, one shaft or the 2 shaft agitator, and its self-cleaning mold of a horizontal type can be used. Furthermore, if it enables it to remove the phenol which prepares a vacuum flash plate tub and carries out a byproduction to the last in the middle of a reaction, it is effective in the second reaction band.

[0022] In this invention, a bivalence hydroxy compound and a carbonate compound are blended as mentioned above, and are dissolved with the reaction temperature of 100-280 degrees C in the first reaction band. Subsequently, the ester exchange reaction of the inert gas is supplied and carried out at a rate of 0.01-2 (weight ratio) to a bivalence hydroxy compound, and the reaction mixture containing a low-molecular-weight polycarbonate is made to generate. Here, the same equipment may perform the dissolution and the reaction of each raw material, and separate equipment may perform them. Moreover, especially the supply approach of inert gas is not restricted, but may be performed from the time of the dissolution of a raw material. And if a reaction rate becomes slow and reaction temperature exceeds 280 degrees C at less than 100 degrees C, side reaction, such as degradation, becomes easy to happen and is not desirable. The phenol which carries out a byproduction by the ester exchange reaction is removed by ordinary pressure, pressurization, or reduced pressure under inert gas circulation. In the continual process of an ester interchange method, in order to return the raw material with which it goes together to a reactor, it is desirable to establish a distilling column in the upper part or the exterior of a reactor.

[0023] Although inert gas is supplied continuously or intermittently and a reaction is advanced in the above-mentioned ester exchange reaction, the amount of inert gas is supplied according to the amount of generation of the phenol which carries out a byproduction. The ester exchange reaction of this amount of inert gas is supplied and carried out at a rate of 0.01-20 (weight ratio) to a bivalence hydroxy compound as above-mentioned. The amount of inert gas cannot fully remove the phenol which carries out a byproduction under by 0.01 (weight/weight). Moreover, if the amount of inert gas exceeds 20 (weight/weight), to the phenol collected, the amount of inert gas will increase and recovery will become difficult. And as for the inert gas supplied, 10 ppm or less of 2 ppm or less of things 0.2 ppm or less are preferably used for the oxygen density in inert gas still more preferably. In case this inert gas is supplied, a pressure is usually -500mmHg-10 kg/cm2. It is good. this invention -- setting -- as inert gas -- N2, and helium, Ar, Ne and CO2 etc. -- although it can be used -- industrial -- N2 It is the most advantageous. The ester exchange reactions of the first reaction band may be any of a continual process or a batch process. And this ester exchange reaction can also divide a reactor or more into two according to the conditions (temperature, pressure, etc.) of equipment if needed. Thus, the reaction mixture with which viscosity average molecular weight contained the low-molecular-weight polycarbonate of 1,000-25,000 is generated by the ester exchange reaction in the first reaction band. Here, if the reaction load in the next second reaction band becomes large and viscosity average molecular weight exceeds 25,000 less than by 1,000, viscosity will become high too much and processing will become difficult in the usual agitator.

[0024] Subsequently, by the manufacture approach of this invention, the target polycarbonate can be obtained by it being higher than the reaction temperature in the first reaction band, and selecting the reaction mixture generated in said first reaction band in 200-350 degrees C, supplying inert gas at a rate of 0.002-1 (weight ratio) to a bivalence hydroxy compound, and carrying out an ester exchange reaction in the second reaction band. When performing the ester exchange reaction in the second reaction band, the reaction temperature is higher than 100-280 degrees C which is the reaction temperature in said first reaction band, and the range of it is 200-350 degrees C. If viscosity is too high, and an ester exchange reaction becomes difficult and the reaction temperature in the second reaction band exceeds 350 degrees C at less than 200 degrees C, it is [degradation of quality] according to side reaction etc. and is not desirable. And also in the second reaction band, if in charge of an ester exchange reaction, the ester exchange reaction of the inert gas is supplied and carried out at a rate of 0.002-10 (weight ratio) to a bivalence hydroxy compound. Here, the amount of inert gas cannot fully remove the phenol which carries out a byproduction under by 0.002 (weight/weight). Moreover, if the amount of inert gas exceeds 10 (weight/weight), it will become difficult to collect the byproduction phenols with which it goes together.

[0025] The byproduction phenol with which it goes in the second reaction band together into inert gas can be condensed by the capacitor, or can collect and carry out a reuse by the usual recovery approaches, such as an adsorption process. Moreover, after removing a byproduction phenol, the reuse of the inert gas can be carried out to the ester exchange reaction in the 1st reaction band. the pressure in the second reaction band -- usually -500mmHg-10 kg/cm2 -- desirable -300mmHg-5 kg/cm2 it is . There is this pressure with the cost quantity of vacuum devices in less than -500 mmHgs, and the leak lump from devices, such as oxygen, may increase further. Moreover, 10kg/cm2 Equipment cost becomes high and is not desirable if it exceeds. The ester exchange reactions of the second reaction band may be any of a continual process or a batch process. And if it is in this ester exchange reaction and has the usual stirring function as a reactor, there will be no limit in form, but since viscosity rises from the first reaction band, what has the stirring function of a hyperviscous mold is good. A horizontal-type agitator, the usual extruder, etc. of one shaft or two shafts can be used for these. Thus, viscosity average molecular weight can obtain the polycarbonate of 10,000-50,000 by performing an ester exchange reaction for the reaction mixture generated in the first reaction band in the second reaction band. And the obtained polycarbonate is corned as it is, or after it adds various additives, it is corned, and shaping of desired mold goods is suitably presented with it.

[0026] In addition, in the manufacture approach of this invention, strictly, although there is nothing what is distinguished, the first reaction band and the second reaction band are set up so that a reaction may be performed efficiently. For this reason, the reaction temperature of the second reaction band is usually set up more highly than the reaction temperature of the first reaction band as aforementioned. Consequently, the appending rate of a bivalence hydroxy compound is the second reaction band, and is usually made into 40 - 100% 4 to 99% in the first reaction band. In addition, the first reaction band and the second reaction band are good as for two processes or more than it according to conditions. And the time amount of the ester exchange reaction in this invention is usually 0.2 - 10 hours that what is necessary is just to carry out until it becomes target molecular weight. Moreover, if in charge of an ester exchange reaction, an antioxidant can be used at all the processes or back process (the second reaction band) of a reaction if needed. As this antioxidant, the Lynn system antioxidants, such as tris (nonylphenyl) phosphite, tris phenyl phosphite, 2-ethylhexyl diphenyl phosphite, trimethyl phosphite, triethyl phosphite, tricresyl phosphite, and thoria reel phosphite, are mentioned, for example. N2 [furthermore,] supplied to each reaction band etc. -- although it may be supplied as it is, when inert gas is beforehand heated before and after reaction temperature in order to

avoid the fall of reaction temperature, and advancing a reaction efficiently, it is desirable.
[0027] In the manufacture approach of this invention, although there is no end clearly as effectiveness by supplying this inert gas, the following reason can be considered. That is, by being contained in inert gas and melt, apparent viscosity can fall and a reaction can be advanced quickly. Moreover, since a gaseous-phase interface increases and a by-product can be removed efficiently, reactivity can be raised. And it sets at a reaction anaphase (the second reaction band), and is an ultra-high vacuum (0.01 - 1torr). Since it does not need, it is guessed that the leak of air etc. can be made for there almost to be nothing etc. If the outline of an example of the manufacture approach of this invention is shown, it will become like drawing 1 .

[0028]
[Example] Furthermore, an example and the example of a comparison explain this invention in detail.
After teaching diphenyl carbonate (diphenyl carbonate) 257g (1.2 mols) to the autoclave (with a helical-type stirring aerofoil) made from stainless steel (SUS316) of 1.4l. of example 1 content volume with 228g (one mol) of bisphenol A and making it fully purge with nitrogen gas, it heated and dissolved in it to 180 degrees C. Subsequently, the temperature up was carried out from 180 degrees C to 220 degrees C, and nitrogen gas was continuously blown into coincidence by 800ml / min (1 g/min). In addition, the temperature up of the nitrogen gas was carried out to 220 degrees C with the heating coil under oil pass. It checked by analysis that a phenol existed soon in the nitrogen gas extracted from the autoclave upper part. The ester exchange reaction was performed for about 2.5 hours, and the reaction mixture was made to generate in this condition. The viscosity average molecular weight of the polycarbonate which this reaction mixture generated was 2,200 and a low-molecular-weight polycarbonate. Then, while carrying out the temperature up from 220 degrees C to 280 degrees C, nitrogen gas was continuously blown by 500ml / min (about 0.63 g/min), and the ester exchange reaction was advanced. This reaction was performed for 3.5 hours and the transparent polycarbonate was obtained on viscosity in the autoclave. As a result of dissolving the obtained polycarbonate in a methylene chloride and measuring viscosity average molecular weight, the viscosity average molecular weight of this polycarbonate was 22,500. The obtained polycarbonate was ground, and it corned and pelletized with the extruder at 220-270 degrees C. Injection molding of this pellet was carried out, and YI (Yellowness Index) and warm water tensile strength of mold goods which were obtained were measured. The obtained result is shown in the 3rd table.
[0029] examples 2-7 and the examples 1-4 of a comparison -- it carried out like the example 1 except having changed a monomer, the amount of nitrogen gas, reaction time, etc. according to the 1st table and the 2nd table, respectively. The obtained result is shown in the 3rd table. In addition, measurement of viscosity average molecular weight, YI, and warm water tensile strength followed the degree.
1) Viscosity average molecular weight (Mv)
After measuring the viscosity of the methylene chloride solution in 20 degrees C and asking for the [limiting viscosity eta] deciliter / g from this with the Ubbelohde viscosity tubing, it computed in the degree type.
[eta] -- =1.23x10-5Mv --] by 0.832YI (Yellowness Index) color meter SM-3[Suga Test Instruments Co., Ltd. -- using -- JIS It measured based on K-7103-77.
3) It is JIS 2 hours [after being immersed in warm water with a warm water tensile strength of 80 degrees C for 16 hours] after. It measured based on K-7113-81.
[0030]
[Table 1]

第 1 表

	原料						触媒	
	(A)	使用量		(B)	使用量		種類	使用量
		(g)	(モル)		(g)	(モル)		(g)
実施例 1	BPA	228	1.0	DPC	257	1.2	無し	−
実施例 2	BPA	228	1.0	DPC	257	1.2	無し	−
実施例 3	DHEB	166	1.0	DPC	257	1.2	無し	−
実施例 4	BPA	228	1.0	DPC	257	1.2	Zn-Ac	0.8
実施例 5	BPA	228	1.0	DPC	257	1.2	無し	−
実施例 6	BPA	228	1.0	DPC	257	1.2	無し	−
実施例 7	BPA	228	1.0	DPC	257	1.2	無し	−
比較例 1	BPA	228	1.0	DPC	257	1.2	無し	−
比較例 2	BPA	228	1.0	DPC	257	1.2	無し	−
比較例 3	DHEB	166	1.0	DPC	257	1.2	無し	−
比較例 4	BPA	228	1.0	DPC	257	1.2	Zn-Ac	0.8

BPA ：ビスフェノールA
DHEB ：ジ（ヒドロキシエチル）ベンゼン
DPC ：炭酸ジフェニル
Zn-Ac ：酢酸亜鉛

[0031]
[Table 2]

第 2 表

	N_2 第一反応帯域		N_2 第二反応帯域		反応条件	
	使用量	(A) に対する比*1	使用量	(A) に対する比*1	温 度 (℃)	時間 (Hr)
実施例 1	800mℓ/min (1.0g/min)	0.66	500mℓ/min (0.63g/min)	0.58	180 220 220～280 280	0.5 2.0 1.0 2.5
実施例 2	100mℓ/min (0.13g/min)	0.10	50mℓ/ min (0.063g/min)	0.66	180 220 220～280 290	0.5 2.5 1.0 3.0
実施例 3	300mℓ/min (0.38g/min)	0.25	300mℓ/min (0.38g/min)	0.034	170 210 210～280 280	0.5 2.0 1.0 3.0
実施例 4	300mℓ/min (0.38g/min)	0.25	300mℓ/min (0.38g/min)	0.034	180 220 220～280 280	0.5 1.5 1.0 2.0
実施例 5	13ml/min*2 (0.016g/min)	0.015	500mℓ/min (0.63g/min)	0.58	180 220 220～280 280	0.5 3.0 1.0 2.5
実施例 6	800mℓ/min (1.0 g/min)	0.66	6.4mℓ/min (0.008g/min)	0.01	180 220 220～280 280	0.5 2.0 1.0 3.5
実施例 7	800mℓ/min (1.0 g/min)	0.66	5.000mℓ/min (6.3g/min)	5.8	180 220 220～280 280	0.5 2.0 1.0 2.5

＊1：N_2 使用量は、全反応時間をT（Hr）として次式より算出
〔N_2 使用量〕×60×〔T／(A) の使用量〕
＊2：Arガスを使用

[0032]
[Table 3]

第 2 表（続き）

	N_2		N_2		反応条件	
	第一反応帯域		第二反応帯域			
	使用量	(A) に対する比*1	使用量	(A) に対する比*1	温 度 (℃)	時間 (Hr)
比較例 1	800mℓ/min (1.0g/min)	0.66	0.1mℓ/min (1.25 ×10^{-4} g/min)	2 × 10^{-4}	180 220 220～280 280	0.5 2.0 1.0 5.0
比較例 2	6mℓ/min (0.008g/min)	0.005	500mℓ/min (0.63g/min)	0.58	180 220 220～280 280	0.5 2.0 1.0 2.5
比較例 3	800mℓ/min (1.0g/min)	0.66	0.87mℓ/min (0.0011g/min)	0.001	180 220 220～280 280	0.5 2.0 1.0 2.5
比較例 4	800mℓ/min (1.0g/min)	0.66	1.5mℓ/min (0.0019g/min)	0.0017	180 220 220～280 280	0.5 2.0 1.0 2.5

[0033]
[Table 4]

第 3 表

	試験結果			
	粘度平均分子量 Mv	YI	温水引張強度（%）	
			前	後
実施例 1	22,500 (2,200)	2.5	105	98
実施例 2	21,300 (1,900)	2.8	98	95
実施例 3	20,500 (1,900)	3.5	102	94
実施例 4	21,800 (3,100)	2.6	98	96
実施例 5	22,600 (2,500)	2.6	105	101
実施例 6	19,800 (2,000)	3.5	98	97
実施例 7	23,000 (3,100)	2.4	100	98
比較例 1	5,800 (2,200)	4.2	—	—
比較例 2	7,800 (560)	3.8	—	—
比較例 3	4,100 (2,100)	8.7	—	—
比較例 4	12,000 (2,400)	6.2	—	—

粘度平均分子量
上段： 第二反応帯域終了後
下段： 第一反応帯域終了後

[0034] It carried out like the example 1 except having taught p-cumyl phenol 6.8g (it being 0.05 mols to bisphenol A) as 228g [of example 8 bisphenol A] (one mol), and diphenyl carbonate 257g (1.2 mols), diphenyl ether 28.2g (0.17 mols, 10 % of the weight), and an end halt agent. The viscosity average molecular weight of the polycarbonate generated in the first reaction band was 1,800 and a low-molecular-weight polycarbonate. It was 20,500 as a result of measuring viscosity average molecular weight similarly on viscosity finally about the transparent polycarbonate which remained in the autoclave.
[0035] It carried out like the example 1 except having prepared the boric acid of 0.018g, 0.18g

of 15% of tetramethylammonium hydroxide water solutions, and 0.003g of sodium hydrogencarbonates as 228g [of example 9 bisphenol A] (one mol), and diphenyl carbonate 257g (1.2 mols), diphenyl ether 28.2g (0.17 mols, 10 % of the weight), and a catalyst. The viscosity average molecular weight of the polycarbonate generated in the first reaction band was 2,100 and a low-molecular-weight polycarbonate. It was 24,000 as a result of measuring viscosity average molecular weight similarly on viscosity finally about the transparent polycarbonate which remained in the autoclave.

[0036] N2 used for the example of comparison 5 second reaction band It carried out like the example 8 except having changed the amount. The viscosity average molecular weight of the polycarbonate generated in the first reaction band was 650 and a low-molecular-weight polycarbonate. It was 9,200 as a result of measuring viscosity average molecular weight similarly about the obtained polycarbonate.

[0037] After teaching 4,000g of bisphenol A to the autoclave (with a support mold stirring aerofoil) made from stainless steel (SUS316) of 15l. of example 10 content volume and making it fully purge with nitrogen gas, it heated and dissolved in it to 180 degrees C. Moreover, after teaching diphenyl carbonate 8,000g to another autoclave of the same size and making it fully purge with nitrogen gas, it heated and dissolved in it to 180 degrees C. Each above-mentioned raw material was continuously supplied to the autoclave (with a helical-type stirring aerofoil) made from stainless steel (SUS316) of 5l. of content volume with the small gear type pump. In the speed of supply, bisphenol A supplied 342g /and diphenyl carbonate in 1,885g /an hour in an hour. Nitrogen gas was supplied to coincidence the rate [pars basilaris ossis occipitalis / of an autoclave] for 1,200ml/(1.51 g/min). In addition, the autoclave was heated at 220 degrees C. Moreover, nitrogen gas was also heated at 220 degrees C. Mixture was continuously extracted from the pars basilaris ossis occipitalis, KRC kneader [Kurimoto, Ltd. make and (2 inches, ratio-of-length-to-diameter=12 and 1.2l.) were supplied, the ester exchange reaction in the first reaction band was performed, and the reaction mixture was made to generate, as it has been about 3 hours about the residence time in an autoclave. In addition, the jacket was heated at 240 degrees C, supplied nitrogen gas to the mixture feed zone by part for 750ml/, and discharged gas from the vent section near a delivery. The viscosity average molecular weight of the polycarbonate generated in the first reaction band was 2,800 and a low-molecular-weight polycarbonate. Subsequently, the obtained reaction mixture was supplied to the KRC kneader of the same size as the above, nitrogen gas was supplied the rate for 750ml/similarly, and the ester exchange reaction was performed. In addition, the KRC kneader heated at 280 degrees C. It was 19,300 as a result of measuring viscosity average molecular weight similarly about the obtained polycarbonate.

[0038] it can set for examples 8-10 and the example 5 of a comparison -- reaction conditions, such as a monomer, an amount of nitrogen gas, and reaction time, are shown in the 4th table and the 5th table, respectively. Moreover, about the polycarbonate obtained in examples 8-10 and the example 5 of a comparison, it fabricated like the example 1 and YI (Yellowness Index) and warm water tensile strength of mold goods were measured. The result is shown in the 6th table.

[0039]

[Table 5]

第 4 表

	原料						触媒	
	(A)	使用量		(B)	使用量		種類	使用量
		(g)	(モル)		(g)	(モル)		(g)
実施例 8	BPA	228	1.0	DPC	257	1.2	無し	−
実施例 9	BPA	228	1.0	DPC	257	1.2	① ② ③	0.0018 0.1 0.003
比較例 5	BPA	228	1.0	DPC	257	1.2	無し	−
実施例10	BPA	342 g/hr (1.5 モル/hr)		DPC	1885g/hr (8.8 モル/hr)		無し	−

実施例 9 の触媒：① ホウ酸
② テトラメチルアンモニウムヒドロキシド
③ 炭酸水素ナトリウム

[0040]
[Table 6]

第 5 表

	N_2 第一反応帯域		N_2 第二反応帯域		反応条件	
	使用量	(A) に対する比*1	使用量	(A) に対する比*1	温 度 (℃)	時間 (Hr)
実施例 8	800mℓ/min (0.1g/min)	0.66	500mℓ/min (0.63g/min)	0.58	180 220 220～280 280	0.5 2.0 1.0 2.5
実施例 9	800mℓ/min (0.1g/min)	0.66	500mℓ/min (0.63g/min)	0.58	180 220 220～280 280	0.5 2.0 1.0 2.5
比較例 5	800mℓ/min (0.1g/min)	0.66	1.5mℓ/min (0.0019g/min)	0.017	180 220 220～280 280	0.5 2.0 1.0 2.5
実施例10	1200mℓ/min (1.5g/min)	0.79	750mℓ／min 750mℓ／min	0.39 0.39	220 240 280	3.0 0.55 0.55

[0041]
[Table 7]

第 6 表

	試 験 結 果			
	粘度平均分子量 Mv	YI	温水引張強度 (%)	
			前	後
実施例 8	20,500 (1,800)	2.8	102	98
実施例 9	24,000 (2,100)	3.1	99	98
比較例 5	9,200 (650)	4.2	−	−
実施例10	19,300 (2,800)	3.2	100	98

[0042]
[Effect of the Invention] As mentioned above, according to this invention, a polycarbonate can be easily obtained by changing the reaction temperature in the first reaction band and the second reaction band, supplying inert gas using a bivalence hydroxy compound and a carbonate compound, and performing ESURU exchange reaction. The polycarbonate obtained by the manufacture approach of this invention is excellent in a hue or a mechanical strength, and is used suitable for an optic, a machine part, electrical machinery and electronic parts, autoparts, etc.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] And a bivalence hydroxy compound is received in inert gas. the first reaction band -- (A) bivalence hydroxy compound and (B) carbonate compound -- the reaction temperature of 100-280 degrees C -- The reaction mixture with which it supplies, an ester exchange reaction is carried out at a rate of 0.01-20 (weight ratio), and viscosity average molecular weight contains the low-molecular-weight polycarbonate of 1,000-25,000 is made to generate. Subsequently In the second reaction band, it is higher than the first reaction band in the reaction temperature of the above-mentioned reaction mixture, and a bivalence hydroxy compound is received in inert gas at 200-350 degrees C. The manufacture approach of the polycarbonate characterized by supplying and carrying out an ester exchange reaction at a rate of 0.002-10 (weight ratio), and viscosity average molecular weight manufacturing the polycarbonate of 10,000-50,000.
[Claim 2] The manufacture approach of a polycarbonate according to claim 1 that the oxygen density in the inert gas used in the first reaction band and the second reaction band is characterized by being 10 ppm or less.
[Claim 3] It is the pressure of the first reaction band and the second reaction band -500 mmHg/cm2 The manufacture approach of the polycarbonate according to claim 1 characterized by considering as the above.

[Translation done.]